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(54) DISPERSIONS DE POLYMERES CATIONIQUES POUR DETERMINER LES FORMATS DE PAPIER
(54) CATIONIC POLYMER DISPERSIONS FOR PAPER SIZING

(57)

The present invention relates to cationic aqueous polymer dispersions comprising small particles which are used for internal sizing and surface sizing of paper, board and cardboard.

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Cationic polymer dispersions for paper sizing

Abstract

The present invention relates to cationic aqueous polymer dispersions comprising small particles which are used for internal sizing and surface sizing of paper, board and cardboard.

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Cationic polymer dispersions for paper sizing

5 The present invention relates to cationic aqueous polymer dispersions comprising small particles which are used for internal sizing and surface sizing of paper, board and cardboard.

10 Polymer dispersions which have cationic charges are preferably used for the internal sizing and surface sizing of paper, board and cardboard, since, owing to their affinity to cellulose fibres, cationic charges particularly readily become attached to them.

15 In principle, two types of aqueous dispersions which have cationic groups and can be used for sizing paper are known. One comprises polymer dispersions which have cationic groups and the other amphoteric polymer dispersions which also have anionic groups in addition to the cationic groups.

20 DE 24 54 397 A discloses cationic aqueous copolymer dispersions prepared by emulsion copolymerization of olefinically unsaturated monomers in the presence of cationic polymeric dispersants. The preparation of the cationic dispersant is effected by solution polymerization of, inter alia, monomers which have quaternary or tertiary nitrogen groups, water-miscible organic solvents preferably being employed, in particular low molecular weight alcohols or acetone being used. When cationic monomers having a tertiary nitrogen atom are used, formic acid is added in addition to the solvents mentioned, in order to introduce the cationic charge. The disadvantage of these dispersions is their high content of readily volatile organic solvents. Owing to their presence, problems relating to occupational hygiene are encountered on drying the paper, which is carried out at temperatures of about 60 - 80°C. Readily volatile organic solvents must therefore be removed from the end product by a distillation step, making the preparation process for these products more expensive.

30 EP 051 144 A states that the cationic aqueous copolymer dispersions disclosed in DE 24 54 397 A are still in need of improvement in their effectiveness as sizes. An

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improvement was achieved by incorporation of an ethylenically unsaturated carboxylic acid or of maleic anhydride as polymerized units, with the result that amphoteric aqueous polymer dispersions were obtained. It is stated that films of dried, amphoteric dispersions are substantially more water-resistant than films of cationic dispersions having a similar composition, as described, for example, in DE 24 54 397 A. However, the presence of a carboxylic acid as polymerized units leads to a greater tendency of the prepared polymer dispersion to foam during the surface sizing of paper.

There was therefore a need for improved polymer dispersions which have a low content of readily volatile organic solvents, exhibit little tendency to foam and have good sizing properties.

Surprisingly, cationic aqueous polymer dispersions which have greater effectiveness than the amphoteric polymer dispersions described in the prior art and contain no readily volatile organic solvents or only small amounts thereof have now been found.

The invention relates to cationic aqueous polymer dispersions comprising small particles, obtainable by polymerization of a monomer mixture consisting of

- a) 20 - 60% by weight of at least one optionally substituted styrene,
- b) 40 - 80% by weight of at least one C₁-C₁₈-(meth)acrylic acid ester and
- c) 0 - 20% by weight of at least one nonionic ethylenically unsaturated monomer differing from a) and b),

the sum of a) + b) + c) being 100% by weight,

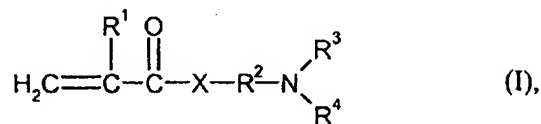
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in the presence of an aqueous polymer dispersion obtainable by a solution polymerization, carried out in a saturated C₁-C₆-carboxylic acid, of a monomer mixture consisting of

- 5 d) 15 - 35% by weight of at least one (meth)acrylic acid ester and/or (meth)-acrylamide which contains a tertiary amino group,
- e) 65 - 85% by weight of at least one optionally substituted styrene and
- 10 f) 0 - 20% by weight of at least one nonionic or cationic ethylenically unsaturated monomer differing from d) and e),
- the sum of d) + e) + f) being 100% by weight.

- 15 The preparation of the polymer dispersion according to the invention is carried out by emulsion polymerization of a monomer mixture a) - c) in the presence of an aqueous polymer dispersion which acts as an emulsifier. The emulsifier is in turn obtained by solution polymerization of the monomer mixture d) - f) in a saturated C₁-C₆-carboxylic acid and is optionally mixed with water after intermediate isolation and/or
- 20 working up.

For the preparation of the emulsifier, (meth)acrylic acid esters or (meth)acrylamides of the formula (I)



- 25 in which

R¹ represents H or methyl,

R² represents a linear C₁-C₄-alkylene radical,

R^3 and R^4 are identical or different and represent C_1 - C_4 -alkyl and

X represents O or NH,

5

are preferably used as monomers of the group d).

In particular, compounds which correspond to the formula (I), in which R^3 and R^4 are identical and represent methyl or ethyl, are used as monomers of the group d).

10

Particularly preferably, compounds of the formula (I) in which X represents NH and R^3 and R^4 are identical and represent methyl or ethyl, are used as monomers of the group d). Those monomers of the group d) which correspond to the formula (I), in which R^1 represents H or methyl, R^2 represents n-propyl, R^3 and R^4 are identical and represent methyl and X represents NH, are very particularly preferably used.

15

For the preparation of the emulsifier, at least one styrene which may be optionally substituted is used as a monomer of the group e). From the series of the substituted styrenes, α -methylstyrene or vinyltoluene is preferably used. Unsubstituted styrene is particularly preferably used.

20

For the preparation of the emulsifier, nonionic or cationic ethylenically unsaturated monomers differing from d) and e) are used as monomers of the group f). Nitriles, such as, for example, acrylonitrile or methacrylonitrile, amides, such as, for example, acrylamide, methacrylamide or N-methylolacrylamide, vinyl compounds, such as, for example, vinyl acetate or vinyl propionate, acrylic acid or methacrylic acid esters of alcohols having 1 - 18 C atoms, such as, for example, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-, iso- and tert-butyl acrylate, n-, iso- and tert-butyl methacrylate, hexyl acrylate, hexyl methacrylate, ethylhexyl acrylate, stearyl acrylate and stearyl methacrylate, or esters of acrylic acid or methacrylic acid which were prepared by reaction with at least one ethylene oxide unit, such as, for example, hydroxyethyl methacrylate or

30

diethylene glycol monomethacrylate, are preferably used. Vinylpyridine or the quaternized ammonium salts which are derived from the formula (I) and can be obtained, for example, by reacting compounds according to the formula (I) with conventional quaternizing reagents, such as, for example, methyl chloride, benzyl chloride, dimethyl sulphate or epichlorohydrin, are particularly preferably used as cationic monomers of the group f), such as, for example, 2-(acryloyloxy)ethyltrimethylammonium chloride, 2-(methacryloyloxy)ethyltrimethylammonium chloride, 3-(acrylamido)propyltrimethylammonium chloride or 3-(methacrylamido)propyltrimethylammonium chloride.

The parts by weight of the monomers mentioned under d) - f) relate to the total amount of the monomers used for the preparation of the emulsifier, the sum of d) + e) + f) being 100% by weight. Preferably, 20 to 30% by weight of d), 70 to 80% by weight of e) and 0 to 10% by weight of f) are used.

The solution polymerization carried out for the preparation of the emulsifier is carried out as a free radical polymerization in a saturated C₁-C₆-carboxylic acid as solvent. Both saturated C₁-C₆-monocarboxylic acids and saturated C₁-C₆-dicarboxylic acids may be used, saturated C₁-C₆-monocarboxylic acids preferably being used. The saturated C₁-C₆-carboxylic acids used optionally carry further substituents, such as, for example, hydroxyl groups. The solution polymerization is preferably carried out in formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, caproic acid, hydroxypropionic acid or hydroxybutyric acid. Mixtures of different saturated C₁-C₆-carboxylic acids may also be used. The solution polymerization is preferably carried out in formic acid, acetic acid, propionic acid or hydroxypropionic acid, particularly preferably in acetic acid. The saturated C₁-C₆-carboxylic acid used preferably contains not more than 20% by weight of water, particularly preferably not more than 10% by weight of water, very particularly preferably not more than 1% by weight of water, based on the total amount of solvent. Very particularly preferably, the solution polymerization is carried out in at least 99% solids acetic acid without admixture of other carboxylic

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acids. The amount of solvent is chosen so that the concentration of the resulting emulsifier solution is 20 to 70% by weight, calculated from the amount of monomers used.

5 The solution polymerization is preferably carried out in the presence of a chain transfer agent. Suitable chain transfer agents are in particular sulphur compounds, such as, for example, thioglycolic acid or mercaptans, such as, for example, ethyl mercaptan, n-butyl mercaptan, tert-butyl mercaptan, n-dodecyl mercaptan or tert-dodecyl mercaptan. Mercaptans are preferably used, particularly preferably C₈-C₁₄-
10 alkyl mercaptans.

The solution polymerization is initiated by a free radical initiator. Peroxo or azo compounds, such as, for example, hydrogen peroxide, sodium peroxodisulphate, potassium peroxodisulphate and ammonium peroxodisulphate, di-tert-butyl peroxide,
15 dibenzoyl peroxide, azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile) or 2,2'-azobis(2-amidinopropane) dihydrochloride, are preferably used as free radical initiators for the solution polymerization. Azo compounds are preferably used, particularly preferably nitriles, such as, for example, azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile) or 2,2'-azobis(2,4-dimethyl-
20 valeronitrile).

The amount of free radical initiator and chain transfer agent when carrying out the solution polymerization is chosen so that an emulsifier having a mass average molecular weight of 5 000 to 100 000 g/mol is obtained. The determination of the
25 molecular weight distribution and of the mass average molecular weight can be carried out by methods known to a person skilled in the art, such as, for example, gel permeation chromatography, light scattering or ultracentrifuging.

The polymerization temperature for the solution polymerization is preferably
30 30-105°C, particularly preferably 70-100°C. The temperature may also be higher if the procedure is carried out under superatmospheric pressure in a pressure-resistant

reactor. The solution polymerization is preferably carried out in an inert gas atmosphere, such as, for example, in a nitrogen atmosphere. Thorough mixing of the reaction batch is advantageous, and suitable stirrers may be used for this purpose. The duration of the polymerization is usually 1-10 h.

5

When carrying out the solution polymerization for the preparation of the emulsifier, the saturated C_1 - C_6 -carboxylic acid is initially introduced completely or partially into the reaction vessel in a preferred embodiment. Monomers, free radical initiators and optionally chain transfer agents are preferably initially introduced completely or partially in the C_1 - C_6 -carboxylic acid or, in another preferred embodiment, are metered in continuously or in a staggered manner into the reaction batch:

10

In a further preferred embodiment of the solution polymerization, the monomers and optionally the chain transfer agent are initially introduced in the C_1 - C_6 -carboxylic acid, and the free radical initiator is metered into the reaction mixture over a specific period. The addition of the free radical initiator can be effected either uniformly or nonuniformly over the metering period.

15

In a further preferred embodiment of the solution polymerization, the acetic acid and optionally the chain transfer agent are initially introduced while the monomers and the free radical initiator are added continuously to the reaction mixture. All metering operations may be effected either uniformly or nonuniformly over the metering period. When a chain transfer agent is used, it is either completely initially introduced or added continuously to the reaction mixture during the polymerization.

20

25

In all abovementioned embodiments, the free radical initiator is added to the reaction batch either in solid, liquid or dissolved form. If the free radical initiator is a solid, the use of a solution of this free radical initiator is preferred. Preferred used solvents are low molecular weight alcohols, such as, for example, isopropanol, low molecular weight ketones, such as, for example, acetone, or the saturated C_1 - C_6 -carboxylic acid used as a solvent. If a solvent differing from the C_1 - C_6 -carboxylic acid employed is

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used for dissolving a free radical initiator present as a solid, amounts such that only a very low content of < 1% of readily volatile solvent is present in the end product are as a rule sufficient. A saturated C₁-C₆-Carboxylic acid, particularly preferably acetic acid, is particularly preferably used for dissolving the free radical initiator which is present as a solid, since the end product is thus completely free of readily volatile organic solvents.

After the end of the solution polymerization, the emulsifier obtained is either isolated or is mixed directly with water. The emulsifier obtained is preferably mixed directly with water, and a homogeneous liquid phase in which the emulsifier is present partially in solution and partially in dispersed form is prepared by stirring. The concentration of the emulsifier in the liquid phase after the addition of water is preferably 2 to 20% by weight, particularly preferably 5 to 15% by weight. This liquid phase can be used directly as an initially introduced mixture for carrying out the emulsion polymerization for the preparation of the cationic aqueous polymer dispersion according to the invention.

The two-stage process can thus be carried out very simply in a one-pot process without the emulsifier having to be isolated or worked up.

The cationic aqueous polymer dispersion according to the invention is prepared by emulsion polymerization of a monomer mixture consisting of a) - c), the aqueous polymer dispersion prepared in the first stage serving as an emulsifier.

For the preparation of the cationic aqueous polymer dispersion according to the invention, styrene and/or substituted styrenes, such as, for example, α -methylstyrene or vinyltoluene, are used as monomers of group a). Unsubstituted styrene is particularly preferably used.

For the preparation of the cationic aqueous polymer dispersion according to the invention, at least one C₁-C₁₈-(meth)acrylic acid ester is used as monomer of the

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group b). Methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-, iso- and tert-butyl acrylate, n-, iso- and tert-butyl methacrylate, hexyl acrylate, hexyl methacrylate, ethylhexyl acrylate, stearyl acrylate and stearyl methacrylate are preferably used. n-Butyl acrylate or binary mixtures which contain between 10 and 90% by weight of n-butyl acrylate are particularly preferably used. Mixtures of n-butyl acrylate and tert-butyl acrylate are very particularly preferably used.

For the preparation of the cationic aqueous polymer dispersion according to the invention, at least one nonionic, ethylenically unsaturated monomer differing from a) and b) is used as monomer of the group c). Nitriles, such as, for example, acrylonitrile or methacrylonitrile, amides, such as, for example, acrylamide, methacrylamide or n-methylolacrylamide, vinyl compounds, such as, for example, vinyl acetate or vinyl propionate, dienes, such as, for example, butadiene or isoprene, and esters of acrylic acid or methacrylic acid and at least one ethylene oxide unit, such as, for example, hydroxyethyl methacrylate or diethylene glycol mono-methacrylate, are preferably used.

The parts by weight of the monomers mentioned under a) - c) relate to the total amount of the monomers used for the preparation of the second stage, the sum of a) + b) + c) being 100% by weight. 30 to 50% by weight of a) and 50 to 70% by weight of b) and 0 to 10% by weight of c) are preferably used.

For the preparation of the cationic aqueous polymer dispersion according to the invention, the monomers a) - c) are preferably metered continuously into the reaction batch, either as a mixture or separately from one another, when carrying out the emulsion polymerization. The addition may be effected uniformly or nonuniformly over the metering period, i.e. at a varying metering rate.

A free radical initiator is used for initiating the emulsion polymerization. Preferably used free radical initiators are peroxo or azo compounds, such as, for example,

potassium peroxodisulphate, sodium peroxodisulphate or ammonium peroxydisulphate, hydrogen peroxide, tert-butyl hydroperoxide, di-tert-butyl peroxide, dibenzoyl peroxide, azobisisobutyronitrile or 2,2'-azobis(2-methylbutyronitrile). Preferably used free radical initiators are water-soluble free radical initiators, particularly preferably hydrogen peroxide. The preferred water-soluble free radical initiators are preferably combined with reducing agents, such as, for example, sodium sulphite, sodium pyrosulphite, sodium bisulphite, sodium dithionite, sodium hydroxymethanesulphinate or ascorbic acid. Furthermore, the preferred water-soluble free radical initiators are preferably combined with heavy metal salts, such as, for example, cerium, manganese or iron(II) salts, to give a redox system. Particularly preferably, hydrogen peroxide is used in combination with a reducing agent and/or with a heavy metal salt. In a further preferred embodiment, ternary initiator systems consisting of water-soluble free radical initiator, reducing agent and heavy metal salt are used, the ternary initiator system comprising hydrogen peroxide, iron(II) sulphate and ascorbic acid being preferred.

Preferably, some of the free radical initiator is initially introduced before the beginning of the monomer feed, and the remainder is added continuously during the polymerization. In a further preferred embodiment, the total amount of the free radical initiator is added continuously, the metering of the free radical initiator and the metering of the monomers preferably beginning simultaneously.

If, in a preferred embodiment of the emulsion polymerization, a water-soluble free radical initiator is combined with a reducing agent, the reducing agent is preferably initially introduced before the beginning of the emulsion polymerization.

If a water-soluble free radical initiator is used in combination with a heavy metal salt for initiating the emulsion polymerization, a complexing agent for complexing the heavy metal salt used is preferably added after the end of the polymerization. Preferred complexing agents are, for example, ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, polyaspartic acid, imino-

disuccinic acid or the corresponding salts of the above-mentioned acids. The amount of complexing agent used depends on the amount of heavy metal salt used and is preferably from 1 to 10 mol per mol of heavy metal ion.

5 In a preferred embodiment, for the preparation of the cationic aqueous polymer dispersion according to the invention, an oil-soluble free radical initiator sparingly soluble in water and intended for subsequent activation is added after the end of the emulsion polymerization for reducing the residual monomer content. Such free radical initiators are compounds which preferably have a water solubility of <1% at
10 room temperature. Organic peroxides, such as, for example, dibenzoyl peroxide, di-tert-butyl peroxide, tert-butyl hydroperoxide, cumyl hydroperoxide or bis-cyclohexyl peroxodicarbonate, are preferably used. By subsequent activation with an oil-soluble free radical initiator sparingly soluble in water, the contents of all residual monomers can be reduced below 100 ppm.

15 The pH of the emulsion polymerization batch is preferably between 2 and 5. The pH can be adjusted before the emulsion polymerization is carried out, by adding acids, bases or buffers. The emulsion polymerization is preferably carried out without further additions of acids, bases or buffers. Before or during the emulsion polymerization, customary low molecular weight nonionic, anionic or cationic
20 emulsifiers may be added for increasing the dispersing effect. Examples of these are sodium alkanesulphonates, sodium alkylsulphates, sodium dodecylbenzenesulphonates, sulfosuccinic acid esters, fatty alcohol ethoxylates, alkylaryl ethoxylates, primary, secondary and tertiary fatty amine salts, quaternary alkylammonium salts, alkylbenzylammonium salts, quaternary amidoamine compounds,
25 alkylpyridinium salts, alkylimidazolinium salts or alkylloxazolinium salts. The emulsion polymerization is preferably carried out without addition of low molecular weight emulsifiers.

30 The polymerization temperature for the emulsion polymerization is preferably 30-100°C, particularly preferably 70-100°C. The temperature may also be higher if a pressure-resistant reactor under superatmospheric pressure is employed. The

emulsion polymerization is preferably carried out in an inert gas atmosphere, such as, for example, in a nitrogen atmosphere. Thorough mixing of the reaction batch is advantageous, and suitable stirrers can be used for this purpose. The duration of the polymerization is usually 0.5-10 h.

5

The concentration of the cationic aqueous polymer dispersion according to the invention is preferably 10 to 40% by weight, particularly preferably 15 to 35% by weight. The viscosity of a 20% solids dispersion is as a rule 3 to 30 mPas, measured at a temperature of 23°C. The mean particle size of a 20% solids dispersion is
10 preferably < 100 nm, particularly preferably 5 to 50 nm. The mean particle size can be determined by methods known to a person skilled in the art, such as, for example, laser correlation spectroscopy, ultracentrifuging or turbidity measurement.

In order to increase the stability of the cationic aqueous polymer dispersion
15 according to the invention to fungal and/or bacterial attack, a biocide is preferably added. Biocides based on isothiazolinones, benzisothiazolinones or biocides based on benzyl alcohol/formaldehyde condensates which release formaldehyde after addition to the aqueous dispersion are preferably used.

20 The dispersions according to the invention are cationic sizing agents which are completely or substantially free of organic solvents and have high effectiveness and little tendency to foam. They can be used for the internal sizing and surface sizing of paper, board and cardboard. The dispersions according to the invention are preferably suitable for the sizing of alum-containing or alum-free papers produced under acidic
25 or neutral conditions and filled with clay, natural or precipitated calcium carbonate, talc, titanium dioxide or other fillers. Suitable fibres are bleached or unbleached, wood-free or wood-containing, wastepaper-containing or deinked pulps. The dispersions according to the invention are particularly suitable for the internal sizing and surface sizing of papers, boards and cardboards comprising wood-containing and
30 wastepaper-containing stocks, such as, for example, corrugated boards and cardboard for packaging purposes, newsprint, or wood-containing printing papers. Often, for example, packaging papers produced from wastepaper are coloured with basic or

cationic dyes, with which the dispersions according to the invention are outstandingly compatible, whereas this is not the case with amphoteric or anionic dispersions.

- 5 In a preferred embodiment, the dispersions according to the invention are used as internal sizing agents since, owing to their cationic charges, they have an affinity to the cellulose fibres and, when added to the paper stock become attached to said fibres. The dispersions according to the invention are preferably added in the wet end of the paper machine, i.e. before the sheet formation with the paper stock, optionally
- 10 in combination with other internal sizing agents. The amount of sizing agent (calculated as polymer solid) is preferably 0.1 to 3% by weight, based on the dry paper stock, in the case of internal sizing. The advantage over the widely used internal sizing agents comprising alkylketene dimer (AKD) or alkenylsuccinic anhydride (ASA) is the development of the full sizing effect immediately after the
- 15 dryer section of the paper machine, whereas a subsequent maturing time is usually required for the development of the full sizing effect in the case of AKD and ASA. Furthermore, the desired degree of sizing can be exactly established through the choice of the added amount, which is very difficult, for example, when AKD is used.
- 20 In a further preferred embodiment, the dispersions according to the invention are used as surface sizing agents. The base papers may be either unsized or presized with customary internal sizing agents, such as, for example, rosin size, AKD or ASA. The application is effected with the aid of customary application units, such as, for example, a sizing agent press, film press, speed sizer or gate roll. If the dispersions
- 25 according to the invention are used as surface sizing agents, preferably 0.1 - 10% by weight are added to the size liquor. The exact amount depends on the presizing of the base paper and on the desired sizing effect. Preferably, the dispersions according to the invention are used as surface sizing agents together with 0 to 20% by weight of starch in the size liquor. The dispersions according to the invention are very
- 30 compatible with customary size press starches, such as, for example, enzymatically or oxidatively degraded or derivatized starches, in particular cationic starches. If the

dispersions according to the invention are used as surface sizing agents, they are outstandingly suitable for use together with dyes, preferably basic or cationic dyes. Furthermore, the dispersions according to the invention are outstandingly suitable for use together with inorganic white pigments. These can be added to the size liquor for
5 improving the printability. Examples of these are natural or precipitated calcium carbonate, clay, barium sulphate, titanium dioxide, talc or annaline.

The high stability of the dispersions according to the invention to electrolytes, such as, for example, sodium chloride, calcium carbonate, magnesium carbonate or
10 aluminium sulphate, is particularly advantageous. The cations and anions from these electrolytes are often contained in size liquors, either as a result of migration from the paper web, as a result of deliberate addition or as a result of introduction with the fresh water used in the paper mill.

15 The dispersions according to the invention impart to the sized papers very good properties with respect to all modern printing processes, in particular when used in the surface. Thus, in the case of inkjet printing, high ink density and brilliance, little strike-through, very crisp edges and little bleeding in combination with smudge resistance and water resistance are required. By surface application of the dispersions
20 according to the invention, these requirements are met very well. With the use of toners, that is to say, for example, in customary copiers and laser printers, high toner adhesion to the printed paper is required. This property, too, is fulfilled in an outstanding manner by surface application of the dispersions according to the invention to, for example, papers presized with AKD by internal sizing. Furthermore,
25 the dispersions according to the invention are suitable, on surface application, for reducing dusting and picking, which is advantageous for all customary printing processes.

Examples**Preparation examples**5 **Example 1**

Preparation of the emulsifier

10 A mixture of 630.75 g of styrene, 239.25 g of N,N-dimethylaminopropylmethacrylamide, 4.5 g of tert-dodecyl mercaptan (95% solids) and 705 g of glacial acetic acid was initially introduced at room temperature into a 2 l flask having a plane-ground joint and a stirrer and jacket heating and was heated to 95°C under a nitrogen atmosphere and with stirring. After the reaction temperature had been reached, a solution of 12.0 g of azobisisobutyronitrile in 80.0 g of acetone was metered
15 uniformly into the reaction solution over a period of 120 min with continuing stirring. The batch was then stirred for a further 120 min at 95°C and then cooled. A part of the batch was discharged, and 279.2 g remained in the apparatus for the preparation of the 2nd stage. A clear polymer solution having a viscosity of 37 200 mPa.s was obtained.

20

Preparation of the cationic polymer dispersion

1 260 g of demineralized water were added at room temperature, while stirring, to the 279.2 g of the emulsifier remaining in the apparatus. The mixture was heated to 85°C
25 under a nitrogen atmosphere and with continuing stirring. A homogeneous, slightly turbid liquid phase was obtained. After the reaction temperature had been reached, the initially introduced mixture was stirred for a further 15 min and then 20.0 g of a 1% strength iron(II) sulphate solution were added. Thereafter, a mixture of 129.5 g of styrene and 92.5 g of n-butyl acrylate, and 64.8 g of a 3% strength hydrogen peroxide
30 solution were metered simultaneously into the reaction mixture over 90 min at a constant rate from separate feeds, the temperature being kept constant. After the end

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of the feeds, the batch was stirred for a further 15 min at 85°C and then 2.0 g of tert-butyl hydroperoxide (80% solids) were added for subsequent activation. After stirring had been carried out for a further 60 min at 85°C, the batch was cooled and 0.9 g of Preventol® D2 and 10.0 g of a 10% strength aqueous Trilon® B solution were added at room temperature.

A polymer dispersion having a solids content of 19.7% was obtained. A 2.5% solid dispersion was prepared by dilution with demineralized water had an extinction of 1.02 at 660 nm.

Example 2

Preparation of the emulsifier

A mixture of 319.3 g of styrene, 115.7 g of N,N-dimethylaminopropylmethacrylamide, 5.2 g of tert-dodecyl mercaptan (95% solids) and 350 g of glacial acetic acid was initially introduced at room temperature into a 2 l flask having a plane-ground joint and a stirrer and jacket heating and was heated to 95°C under a nitrogen atmosphere and with stirring. After the reaction temperature had been reached, a solution of 4.3 g of 2,2'-azobis(2-methylbutyronitrile) in 40.0 g of acetone was metered uniformly into the reaction solution over a period of 120 min with continuing stirring. The batch was then stirred for a further 120 min at 95°C and then cooled. A part of the batch was discharged, and 280.5 g remained in the apparatus for the preparation of the 2nd stage. A clear polymer solution having a viscosity of 12 300 mPa.s was obtained.

Preparation of the cationic polymer dispersion

1 228 g of demineralized water were added at room temperature, while stirring, to the 280.5 g of the emulsifier remaining in the apparatus. The mixture was heated to 85°C under a nitrogen atmosphere and with continuing stirring. A homogeneous, slightly

turbid liquid phase was obtained. After the reaction temperature had been reached, the initially introduced mixture was stirred for a further 15 min and then 4.0 g of a 1% strength iron(II) sulphate solution were added. Thereafter, a mixture of 88.8 g of styrene, 74.0 g of n-butyl acrylate and 61.05 g of tert-butyl acrylate, and 65.3 g of a 3% strength hydrogen peroxide solution were metered simultaneously into the reaction mixture over 90 min at a constant rate from separate feeds, the temperature being kept constant. After the end of the feeds, the batch was stirred for a further 15 min at 85°C and then 2.0 g of tert-butyl hydroperoxide (80% solids) were added for subsequent activation. After stirring had been carried out for a further 60 min at 85°C, the batch was cooled and 0.9 g of Preventol® D2 were added at room temperature.

A polymer dispersion having a solids content of 20.2% and an extinction of 0.42 (measured at 660 nm on an aqueous sample diluted to 2.5%) was obtained.

Example 3

Preparation of the emulsifier

A mixture of 324.0 g of styrene, 111.0 g of N,N-dimethylaminoethyl methacrylate, 0.6 g of tert-dodecyl mercaptan (95% solids) and 330 g of glacial acetic acid was initially introduced at room temperature into a 2 l flask having a plane-ground joint and a stirrer and jacket heating and was heated to 95°C under a nitrogen atmosphere and with stirring. After the reaction temperature had been reached, a solution of 5.0 g of azobisisobutyronitrile in 60.0 g of acetone was metered into the reaction solution over a period of 120 min with continuing stirring. The batch was then stirred for a further 120 min at 85°C and then cooled. A part of the batch was discharged, and 272.3 g remained in the apparatus for the preparation of the 2nd stage. A clear polymer solution having a viscosity of 26 300 mPa.s was obtained.

Preparation of the cationic polymer dispersion

1 253 g of demineralized water were added at room temperature, while stirring, to the
272.3 g of the emulsifier remaining in the apparatus. The mixture was heated to 85°C
5 under a nitrogen atmosphere and with continuing stirring. A homogeneous, slightly
turbid liquid phase was obtained. After the reaction temperature had been reached,
the initially introduced mixture was stirred for a further 15 min and then 20.0 g of a
1% strength iron(II) sulphate solution were added. Thereafter, a mixture of 112.9 g of
10 styrene, 56.4 g of n-butyl acrylate and 56.4 g of tert-butyl acrylate, and 65.8 g of a
3% strength hydrogen peroxide solution were metered simultaneously into the
reaction mixture over 90 min at a constant rate from separate feeds, the temperature
being kept constant. After the end of the feeds, the batch was stirred for a further 15
min at 85°C and then 2.0 g of tert-butyl hydroperoxide (80% solids) were added for
subsequent activation. After stirring had been carried out for a further 60 min at
15 85°C, the batch was cooled and 0.9 g of Preventol® D2 and 10.0 g of a 10% strength
aqueous Trilon® B solution were added at room temperature.

A polymer dispersion having a solids content of 19.8% and an extinction of 1.05
(measured at 660 nm on an aqueous sample diluted to 2.5%) was obtained.

20

Example 4

Preparation of the emulsifier

25 A mixture of 324.0 g of styrene, 76.2 g of N,N-dimethylaminoethyl methacrylate,
48.3 g of 2-(acryloyloxy)ethyltrimethylammonium chloride (as an 80% strength
aqueous solution) and 0.6 g of tert-dodecyl mercaptan (95% solids) and 330 g of
glacial acetic acid was initially introduced at room temperature into a 2 l flask having
a plane-ground joint and a stirrer and jacket heating and was heated to 95°C under a
30 nitrogen atmosphere and with stirring. After the reaction temperature had been
reached, a solution of 3.0 g of azobisisobutyronitrile in 60.0 g of acetone was

uniformly metered into the reaction solution over a period of 120 min with continuing stirring. The batch was then stirred for a further 120 min at 95°C and then cooled. A part of the batch was discharged, and 277.5 g remained in the apparatus for the preparation of the 2nd stage. A clear polymer solution having a viscosity of
5 17 400 mPa.s was obtained.

Preparation of the cationic polymer dispersion

1 249 g of demineralized water were added at room temperature, while stirring, to the
10 277.5 g of the emulsifier remaining in the apparatus. The mixture was heated to 85°C under a nitrogen atmosphere and with continuing stirring. A homogeneous, slightly turbid liquid phase was obtained. After the reaction temperature had been reached, the initially introduced mixture was stirred for a further 15 min and then 20.0 g of a 1% strength iron(II) sulphate solution were added. Thereafter, a mixture of 112.9 g of
15 styrene, 56.4 g of n-butyl acrylate and 56.4 g of tert-butyl acrylate, and 65.8 g of a 3% strength hydrogen peroxide solution were metered simultaneously into the reaction mixture over 90 min at a constant rate from separate feeds, the temperature being kept constant. After the end of the feeds, the batch was stirred for a further 15 min at 85°C and then 2.0 g of tert-butyl hydroperoxide (80% solids) were added for
20 subsequent activation. After stirring had been carried out for a further 60 min at 85°C, the batch was cooled and 0.9 g of Preventol® D2 and 10.0 g of a 10% strength aqueous Trilon® B solution were added at room temperature.

A polymer dispersion having a solids content of 19.8% and an extinction of 0.93
25 (measured at 660 nm on an aqueous sample diluted to 2.5%) was obtained.

Example 5

Preparation of the emulsifier

5 A mixture of 638.6 g of styrene, 231.4 g of N,N-dimethylaminopropylmethacryl-
amide, 10.4 g of tert-dodecyl mercaptan (95% solids) and 550 g of glacial acetic acid
was initially introduced at room temperature into a 2 l flask having a plane-ground
joint and a stirrer and jacket heating and was heated to 95°C under a nitrogen
10 atmosphere and with stirring. After 95°C had been reached, a solution of 12.8 g of
azobisisobutyronitrile in 230 g of glacial acetic acid was metered uniformly into the
reaction solution over a period of 120 min with continuing stirring. The batch was
then stirred for a further 120 min at 95°C and then cooled. A part of the batch was
discharged, and 275.8 g remained in the apparatus for the preparation of the 2nd
stage. A clear polymer solution having a viscosity of 73 000 mPa.s was obtained.

15

Preparation of the cationic polymer dispersion

1 223 g of demineralized water were added at room temperature, while stirring, to the
275.8 g of the emulsifier remaining in the apparatus. The mixture was heated to 85°C
20 under a nitrogen atmosphere and with continuing stirring. A homogeneous, slightly
turbid liquid phase was obtained. After the reaction temperature had been reached,
the initially introduced mixture was stirred for a further 15 min and then 4.0 g of a
1% strength iron(II) sulphate solution were added. Thereafter, a mixture of 88.8 g of
styrene, 67.5 g of n-butyl acrylate and 67.5 g of tert-butyl acrylate, and 78.3 g of a
25 3% strength hydrogen peroxide solution were metered simultaneously into the
reaction mixture over 90 min at a constant rate from separate feeds, the temperature
being kept constant. After the end of the feeds, the batch was stirred for a further
15 min at 85°C and then 3.0 g of tert-butyl hydroperoxide (80% solids) were added
for subsequent activation. After stirring had been carried out for a further 60 min at
30 85°C, the batch was cooled and 0.9 g of Preventol® D2 were added at room
temperature.

A polymer dispersion having a solids content of 19.8% and an extinction of 0.64 (measured at 660 nm on an aqueous sample diluted to 2.5%) was obtained.

5 **Example 6**

Preparation of the emulsifier

10 A mixture of 604.0 g of styrene, 266.0 g of N,N-dimethylaminoethyl methacrylate and 1.2 g of tert-dodecyl mercaptan (95% solids) and 660 g of glacial acetic acid was initially introduced at room temperature into a 2 l flask having a plane-ground joint and a stirrer and jacket heating and was heated to 85°C under a nitrogen atmosphere and with stirring. After 85°C had been reached, a solution of 10.1 g of azobisisobutyronitrile in 120 g of acetone was uniformly metered into the reaction solution
15 over a period of 120 min with continuing stirring. The batch was then stirred for a further 120 min at 85°C and then cooled. A part of the batch was discharged, and 272.3 g remained in the apparatus for the preparation of the 2nd stage. A clear polymer solution having a viscosity of 70 000 mPa.s was obtained.

20 Preparation of the cationic polymer dispersion

1 253 g of demineralized water were added at room temperature, while stirring, to the 272.3 g of the emulsifier remaining in the apparatus. The mixture was heated to 85°C under a nitrogen atmosphere and with continuing stirring. A homogeneous, slightly
25 turbid liquid phase was obtained. After the reaction temperature had been reached, the initially introduced mixture was stirred for a further 15 min and then 20.0 g of a 1% strength iron(II) sulphate solution were added. Thereafter, a mixture of 112.9 g of styrene, 94.0 g of n-butyl acrylate and 18.8 g of methyl methacrylate, and 65.8 g of a 3% strength hydrogen peroxide solution were metered simultaneously into the
30 reaction mixture over 90 min at a constant rate from separate feeds, the temperature of 85°C being kept constant. After the end of the feeds, the batch was stirred for a

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further 15 min at 85°C and then 2.0 g of tert-butyl hydroperoxide (80% solids) were added for subsequent activation. After stirring had been carried out for a further 60 min at 85°C, the batch was cooled and 0.9 g of Preventol® D2 and 10.0 g of a 10% strength aqueous Trilon® B solution were added.

5

A polymer dispersion having a solids content of 19.8% and an extinction of 0.71 (measured at 660 nm on an aqueous sample diluted to 2.5%) was obtained.

Example 7

10

Preparation of the emulsifier

A mixture of 319.3 g of styrene, 115.7 g of N,N-dimethylaminopropylmethacrylamide, 5.2 g of tert-dodecyl mercaptan (95% solids) and 350 g of glacial acetic acid was initially introduced at room temperature into a 2 l flask having a plane-ground joint and a stirrer and jacket heating and was heated to 95°C under a nitrogen atmosphere and with stirring. After the reaction temperature had been reached, a solution of 6.4 g of azobisisobutyronitrile in 40.0 g of acetone was metered uniformly into the reaction solution over a period of 120 min with continuing stirring. The batch was then stirred for a further 120 min at 95°C and then cooled. A part of the batch was discharged, and 275.8 g remained in the apparatus for the preparation of the 2nd stage. A clear polymer solution having a viscosity of 15 900 mPa.s was obtained.

25 Preparation of the cationic polymer dispersion

1 232 g of demineralized water were added at room temperature, while stirring, to the 275.8 g of the prepolymer remaining in the apparatus. The mixture was heated to 85°C under a nitrogen atmosphere and with continuing stirring. A homogeneous, slightly turbid liquid phase was obtained. After the reaction temperature had been reached, the initially introduced mixture was stirred for a further 15 min and then

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- 4.0 g of a 1% strength iron(II) sulphate solution were added. Thereafter, a mixture of 103.0 g of styrene, 60.4 g of n-butyl acrylate and 60.4 g of tert-butyl acrylate, and 78.3 g of a 3% strength hydrogen peroxide solution were metered simultaneously into the reaction mixture over 90 min at a constant rate from separate feeds, the temperature being kept constant. After the end of the feeds, the batch was stirred for a further 15 min at 85°C and then 3.0 g of tert-butyl hydroperoxide (80% solids) were added for subsequent activation. After stirring had been carried out for a further 60 min at 85°C, the batch was cooled and 0.9 g of Preventol® D2 was added.
- 10 A polymer dispersion having a solids content of 20.0% and an extinction of 0.60 (measured at 660 nm on an aqueous sample diluted 1:10) was obtained.

Example 8

15 Preparation of the emulsifier

- A mixture of 119.0 g of styrene, 43.0 g of N,N-dimethylaminopropylmethacrylamide, 90 g of glacial acetic acid and 1.5 g of azobisisobutyronitrile was initially introduced, at room temperature, into a 2 l flask having a plane-ground joint and a stirrer and jacket heating and was heated to 85°C under a nitrogen atmosphere and with stirring. After the reaction temperature had been reached, stirring was carried out for a further 30 min and a solution of 1.9 g of azobisisobutyronitrile in 11 g of acetone was then metered uniformly into the reaction solution over a period of 60 min. The batch was then stirred for a further 30 min at 85°C and then 875 g of demineralized water were added. For dissolution of the polymer, stirring was carried out for a further 35 min at 65-85°C, followed by cooling.

Preparation of the cationic polymer dispersion

- 30 The emulsifier from stage 1, heated to 85°C, was first stirred for 15 min and then 6 g of a 1% strength iron(II) sulphate solution and 30.0 g of a 6% strength hydrogen

peroxide solution were added in succession. Thereafter, a mixture of 99.0 g of styrene, 94.5 g of n-butyl acrylate and 94.5 g of tert-butyl acrylate, and 120.0 g of a 6% strength hydrogen peroxide solution, were metered into the reaction mixture simultaneously over 120 min at a constant rate from separate feeds, the temperature being kept constant. After the end of the feeds, the batch was stirred for a further 60 min at 85°C and then cooled, and 1.6 g of Preventol® D2 were then added.

A polymer dispersion having a solids content of 28.2% and an extinction of 2.24 (measured at 660 nm on an aqueous sample diluted 1:10) was obtained.

Comparative example 1 according to the teaching of EP 051 144 A

The preparation was carried out analogously to Example 7.

Preparation of the 1st stage:

A mixture of 319.3 g of styrene, 80.7 g of N,N-dimethylaminopropylmethacrylamide, 35.0 g of acrylic acid, 5.2 g of tert-dodecyl mercaptan (95%) and 350 g of glacial acetic acid was initially introduced at room temperature into a 2 l flask having a plane-ground joint and a stirrer and jacket heating and was heated to 95°C under a nitrogen atmosphere and with stirring. After the reaction temperature had been reached, a solution of 6.4 g of azobisisobutyronitrile in 40.0 g of acetone was then metered uniformly into the reaction solution over a period of 120 min with continuing stirring. The batch was then stirred for a further 120 min at 95°C and then cooled. A part of the batch was discharged, and 275.8 g remained in the apparatus for the preparation of the 2nd stage. A clear polymer solution having a viscosity of 20 600 mPa.s was obtained.

Preparation of the 2nd stage:

1 232 g of demineralized water were added at room temperature, while stirring, to the
 275.8 g from the 1st stage which remained in the apparatus. The mixture was heated
 5 to 85°C under a nitrogen atmosphere and with continuing stirring. A homogeneous,
 turbid liquid phase was obtained. After the reaction temperature had been reached,
 the initially introduced mixture was stirred for a further 15 min and then 4.0 g of a
 1% strength iron(II) sulphate solution were added. Thereafter, a mixture of 103.0 g of
 styrene, 60.4 g of n-butyl acrylate and 60.4 g of tert-butyl acrylate, and 78.3 g of a
 10 3% strength hydrogen peroxide solution were metered simultaneously into the
 reaction mixture over 90 min at a constant rate from separate feeds, the temperature
 being kept constant. After the end of the feeds, the batch was stirred for a further 15
 min at 85°C and then 3.0 g of tert-butyl hydroperoxide (80% solids) were added for
 subsequent activation. After stirring had been carried out for a further 60 min at
 15 85°C, the batch was cooled and 0.9 g of Preventol® D2 was added.

A polymer dispersion having a solids content of 20.2% and an extinction of 0.67
 (measured at 660 nm on an aqueous sample diluted 1:10) was obtained.

20 Comparative example 2 according to the teaching of EP 051 144 A

The preparation was effected analogously to Example 8.

Preparation of the 1st stage, analogously to Example 1, EP 051 144 A

25 A mixture of 90.0 g of styrene, 49.5 g of N,N-dimethylaminopropylmethacrylamide,
 22.5 g of acrylic acid, 90.0 g of glacial acetic acid and 1.5 g of azobisisobutyronitrile
 was initially introduced, at room temperature, into a 2 l flask having a plane-ground
 joint and a stirrer and jacket heating and was heated to 85°C under a nitrogen
 30 atmosphere and with stirring. After the reaction temperature had been reached,
 stirring was carried out for a further 30 min and a solution of 1.9 g of azobisiso-

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butyronitrile in 11.0 g of acetone was then metered uniformly into the reaction solution over a period of 60 min. The batch was then stirred for a further 30 min at 85°C and then 875 g of demineralized water were added. For dissolution of the polymer, stirring was carried out for a further 55 min at 65-85°C, followed by cooling.

Preparation of the 2nd stage:

The polymer solution from stage 1, heated to 85°C, was first stirred for 15 min and then 6.0 g of a 1% strength iron(II) sulphate solution and 30.0 g of a 6% strength hydrogen peroxide solution were added in succession. Thereafter, a mixture of 99.0 g of styrene, 94.5 g of n-butyl acrylate and 94.5 g of tert-butyl acrylate, and 120 g of a 6% strength hydrogen peroxide solution, were metered into the reaction mixture simultaneously over 120 min at a constant rate from separate feeds, the temperature being kept constant. After the end of the feeds, the batch was stirred for a further 60 min at 85°C and then cooled, and 1.6 g of Preventol[®] D2 were then added.

A polymer dispersion having a solids content of 29.1% and an extinction of 2.12 (measured at 660 nm on an aqueous sample diluted 1:10) was obtained.

Use examples**Sizing effect**

5 The surface treatment of various test papers with the dispersions according to the invention and the comparative dispersions was effected using a laboratory size press from the firm Mathis, Zürich, Type HF. The size press liquor contained 5 parts by weight of an oxidized potato starch (Perfectamyl® A 4692) and 0.4 - 1.2 parts of the dispersions from Examples 1 - 8 and from Comparative examples 1 - 2, made up to
10 100 parts with water. The test papers were passed 1 - 3 times through the size press liquor in order in each case to achieve an adequate size pick-up. Here, size pick-up is to be understood as meaning the amount of size press liquor in per cent, based on the dry paper stock, which was absorbed by said paper stock, optionally after a plurality of passes through the size press.

15

The sizing effect of the dispersions according to the invention and of the comparative dispersions was tested on the following papers:

20 Paper a): unsized filler-containing coating base paper, basis weight 80 g/m², size pick-up 53% (Examples 1 - 4 and Example 6) or 68% (Example 5). Paper a) was passed once through the size press for treatment per liquor batch. The size pick-up is based on this.

25 Paper b): unsized paper comprising 100% of mixed wastepaper, basis weight 120 g/m², size pick-up 60 %. Paper b) was passed three times through the size press for treatment per liquor batch. The size pick-up is based on this.

30 Paper c): unsized testliner comprising 100% of mixed wastepaper, basis weight 115 g/m², size pick-up 45%. Paper c) was passed twice through the

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size press for treatment per liquor batch. The size pick-up is based on this.

5 Paper d): unsized lining board comprising 100% of mixed wastepaper, basis weight 190 g/m², size pick-up 29%. Paper d) was passed twice through the size press for treatment per liquor batch. The size pick-up is based on this.

10 The drying of the surface-sized papers was effected on a drying cylinder in the course of one minute at 90°C. The papers were then conditioned for 2 hours under standard climatic conditions (23°C, 50% relative humidity) before the degree of sizing was determined.

15 In order to assess the degree of sizing of the surface-sized papers, the Cobb₆₀ values were determined according to DIN 53122. The Cobb₆₀ value is defined as the water absorption of the paper sheet in g/m² after contact with water and after a contact time of 60 s. The lower this value, the better the degree of sizing of the respective paper.

20 The Cobb₆₀ values of the dispersions from Examples 1 - 6 are summarized in Table 1.

Table 1

25 Results of the sizing test, papers a) and b) with the dispersions according to the invention

		Example 1		Example 2		Example 3		Example 4		Example 5		Example 6	
Solids content	%	19.7		20.0		19.8		19.8		19.8		19.8	
Amount used, solid	%	0.16	0.24	0.16	0.24	0.16	0.24	0.16	0.24	0.16	0.24	0.16	0.24
Cobb test													
Paper a)	g/m ²	58	22.9	39	22.7	33	25.6	33	25.8	55	23.6	35	25.8
Paper b)	g/m ²	33	23.0	24.4	21.7	26.9	24.4	26.9	23.3	22.6	20.3	42.0	24.7

The Cobb₆₀ values of the dispersions from Examples 7, 8 and Comparative examples 1, 2 are shown in Table 2.

Table 2

5

Results of the sizing test. Comparison of the dispersions according to the invention with Comparative dispersions 1 and 2, papers c) and d)

		Example 7			Comparative example 1			Example 8			Comparative example 2		
Solids content	%	20.0			20.2			28.2			29.1		
Amount used, solid	%	0.12	0.18	0.24	0.12	0.18	0.24	0.12	0.18	0.24	0.12	0.18	0.24
Cobb test Paper c)	g/m ²	31	20	-	49	23.5	-	26.7	18.7	-	29.3	19.0	-
Paper d)	g/m ²	-	30	21	-	59	25.1	-	25.6	20.8	-	59	22.1

10 The dispersion of Comparative example 1 shows poorer sizing properties compared with Example 7, as does the dispersion of Comparative example 2 compared with Example 8.

Tendency to foam

15

The tendency to foam formation was determined as follows:

250 ml each of a size press liquor from Example 5 and Comparative example 2 were introduced into a cylinder (height: 42 cm, diameter: 6 cm). The size press liquors contained in each case 5% by weight of Perfectamyl® A4692 and 1% by weight of polymer dispersion according to Example 5 and Comparative example 2, respectively. Foam was produced by means of a small propeller (1 000 rpm) and by passing in air (400 ml/min). After 2 minutes, the air supply was stopped and the stirrer was switched off. The resulting amount of foam was read:

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Example 5: Amount of foam 110 ml; Comparative example 2: Amount of foam 140 ml.

5 Thus, the size liquor prepared using the dispersions according to the invention exhibits an amount of foam which is 21.5% lower than the size liquor prepared using the dispersion of the prior art.

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CLAIMS:

1. A cationic aqueous polymer dispersion comprising small particles, obtainable by polymerization of a monomer mixture consisting of:

5 (a) 20-60% by weight of at least one optionally substituted styrene;

(b) 40-80% by weight of at least one C₁-C₁₈-(meth)acrylic acid ester; and,

(c) 0-20% by weight of at least one nonionic
10 ethylenically unsaturated monomer differing from (a) and (b),

the sum of (a) + (b) + (c) being 100% by weight,

in the presence of an emulsifier which is an aqueous polymer dispersion obtainable by a solution polymerization, carried
15 out in a saturated C₁-C₆-carboxylic acid, of a monomer mixture consisting of:

(d) 15-35% by weight of at least one (meth)acrylic acid ester and/or (meth)acrylamide which contains a tertiary amino group;

20 (e) 65-85% by weight of at least one optionally substituted styrene; and,

(f) 0-20% by weight of at least one nonionic or cationic ethylenically unsaturated monomer differing from (d) and (e),

25 the sum of (d) + (e) + (f) being 100% by weight.

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2. The cationic aqueous polymer dispersion according to claim 1, wherein the C₁-C₆-carboxylic acid is a monocarboxylic acid.

3. The cationic aqueous polymer dispersion according to claim 1, wherein the C₁-C₆-carboxylic acid is acetic acid.

4. The cationic aqueous polymer dispersion according to claim 3, wherein the acetic acid contains not more than 20% by weight of water.

5. The cationic aqueous polymer dispersion according to any one of claims 1 to 4, wherein the emulsifier is a 2-20% strength by weight aqueous polymer dispersion.

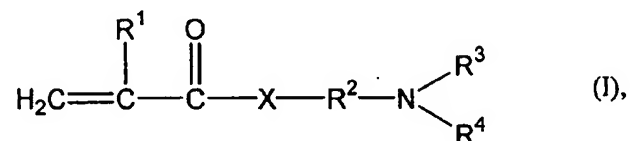
6. The cationic aqueous polymer dispersion according to any one of claims 1 to 4, wherein the emulsifier is a 5-15% strength by weight aqueous polymer dispersion.

7. The cationic aqueous polymer dispersion according to any one of claims 1 to 6, wherein the monomers (a) and (e) are unsubstituted styrene.

8. The cationic aqueous polymer dispersion according to any one of claims 1 to 7, wherein 30-50% by weight of monomer (a) is used and 70-80% by weight of monomer (e) is used.

9. The cationic aqueous polymer dispersion according to any one of claims 1 to 8, wherein monomer (d) is a monomer of the formula (I)

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in which

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R^1 is H or methyl,

R^2 is a linear C_1 - C_4 -alkylene radical,

R^3 and R^4 are identical or different and are C_1 - C_4 -alkyl, and

X is O or NH.

5 10. The cationic aqueous polymer dispersion according to any one of claims 1 to 9, wherein 20-30% by weight of monomer (d) is used.

11. The cationic aqueous polymer dispersion according to any one of claims 1 to 10, wherein monomer (b) is at
 10 least one compound selected from the group consisting of methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-butyl acrylate, iso-butyl acrylate, tert-butyl acrylate, n-butyl methacrylate, iso-butyl methacrylate, tert-butyl
 15 methacrylate, hexyl acrylate, hexyl methacrylate, ethylhexyl methacrylate, stearyl acrylate and stearyl methacrylate.

12. A process for preparing a cationic aqueous polymer dispersion as defined in claim 1 comprising the steps of:

(i) preparing a polymer dispersion by solution
 20 polymerization of a monomer mixture consisting of

(d) 15-35% by weight of at least one (meth)acrylic acid ester and/or (meth)acrylamide which contains a tertiary amino group,

(e) 65-85% by weight of at least one
 25 optionally substituted styrene, and

(f) 0-20% by weight of at least one nonionic or cationic ethylenically unsaturated monomer differing from (d) and (e),

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the sum of (d) + (e) + (f) being 100% by weight,
in at least one saturated C₁-C₆-carboxylic acid;

(ii) adding water to the polymer dispersion to prepare
an aqueous polymer dispersion which acts as an emulsifier;

5 and,

(iii) emulsion polymerizing a monomer mixture consisting
of

(a) 20-60% by weight of at least one
optionally substituted styrene,

10 (b) 40-80% by weight of at least one
C₁-C₁₈-(meth)acrylic acid ester, and

(c) 0-20% by weight of at least one nonionic
ethylenically unsaturated monomer differing from (a) and
(b),

15 the sum of (a) + (b) + (c) being 100% by weight,
in the presence of the emulsifier.

13. The process according to claim 12, wherein an oil-
soluble free radical initiator sparingly soluble in water is
added for subsequent activation after the end of the
20 emulsion polymerization step (iii).

14. The process according to claim 12 or 13, wherein
the C₁-C₆-carboxylic acid is a monocarboxylic acid.

15. The process according to claim 12 or 13, wherein
the C₁-C₆-carboxylic acid is acetic acid.

25 16. The process according to claim 15, wherein the
acetic acid contains not more than 20% by weight of water.

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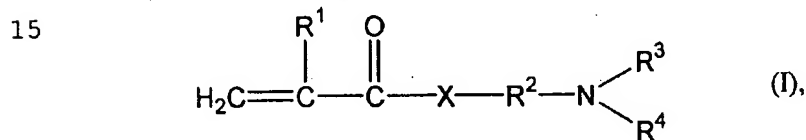
17. The process according to any one of claims 12 to 16, wherein the emulsifier is a 2-20% strength by weight aqueous polymer dispersion.

18. The process according to any one of claims 12 to 17, wherein the emulsifier is a 5-15% strength by weight aqueous polymer dispersion.

19. The process according to any one of claims 12 to 18, wherein the monomers (a) and (e) are unsubstituted styrene.

20. The process according to any one of claims 12 to 19, wherein 30-50% by weight of monomer (a) is used and 70-80% by weight of monomer (e) is used.

21. The process according to any one of claims 12 to 20, wherein monomer (d) is a monomer of the formula (I)



in which

R^1 is H or methyl,

R^2 is a linear C_1 - C_4 -alkylene radical;

20 R^3 and R^4 are identical or different and are C_1 - C_4 -alkyl, and

X is O or NH.

22. The process according to any one of claims 12 to 21, wherein 20-30% by weight of monomer (d) is used.

23. The process according to any one of claims 12 to 22, wherein monomer (b) is at least one compound selected from the group consisting of methyl acrylate, methyl

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methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-butyl acrylate, iso-butyl acrylate, tert-butyl acrylate, n-butyl methacrylate, iso-butyl methacrylate, tert-butyl methacrylate, hexyl acrylate, 5 hexyl methacrylate, ethylhexyl methacrylate, stearyl acrylate and stearyl methacrylate.

24. Use of an aqueous polymer dispersion obtainable by a solution polymerization, carried out in a saturated C₁-C₆-carboxylic acid, of a monomer mixture consisting of:

10 (d) 15-35% by weight of at least one (meth)acrylic acid ester and/or (meth)acrylamide which contains a tertiary amino group;

(e) 65-85% by weight of at least one optionally substituted styrene; and,

15 (f) 0-20% by weight of at least one nonionic or cationic ethylenically unsaturated monomer differing from (d) and (e),

the sum of (d) + (e) + (f) being 100% by weight,

as an emulsifier in an emulsion polymerization.

20 25. Use of an aqueous polymer dispersion obtainable by a solution polymerization, carried out in a saturated C₁-C₆-carboxylic acid, of a monomer mixture consisting of:

(d) 15-35% by weight of at least one (meth)acrylic acid ester and/or (meth)acrylamide which 25 contains a tertiary amino group;

(e) 65-85% by weight of at least one optionally substituted styrene; and,

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(f) 0-20% by weight of at least one nonionic or cationic ethylenically unsaturated monomer differing from (d) and (e),

the sum of (d) + (e) + (f) being 100% by weight,

5 as an emulsifier in emulsion polymerization of a monomer mixture consisting of

(a) 20-60% by weight of at least one optionally substituted styrene,

(b) 40-80% by weight of at least one
10 C₁-C₁₈-(meth)acrylic acid ester, and

(c) 0-20% by weight of at least one nonionic ethylenically unsaturated monomer differing from (a) and (b),

the sum of (a) + (b) + (c) being 100% by weight.

15 26. The use according to claim 25, wherein monomer (b) is at least one compound selected from the group consisting of methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-butyl acrylate, iso-butyl acrylate, tert-butyl acrylate, n-
20 butyl methacrylate, iso-butyl methacrylate, tert-butyl methacrylate, hexyl acrylate, hexyl methacrylate, ethylhexyl methacrylate, stearyl acrylate and stearyl methacrylate.

27. The use according to claim 25 or 26, wherein the monomer (a) is unsubstituted styrene.

25 28. The use according to any one of claims 25 to 27, wherein 30-50% by weight of monomer (a) is used.

29. The use according to any one of claims 24 to 28, wherein the monomer (e) is unsubstituted styrene.

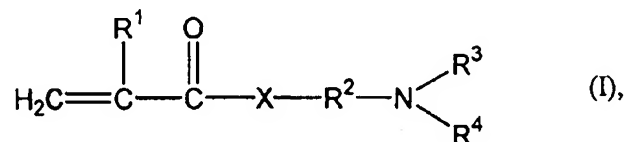
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30. The use according to any one of claims 24 to 29, wherein 70-80% by weight of monomer (e) is used.

31. The use according to any one of claims 24 to 30, wherein 20-30% by weight of monomer (d) is used.

5 32. The use according to any one of claims 24 to 31, wherein monomer (d) is a monomer of the formula (I)



in which

10 R^1 is H or methyl,

R^2 is a linear C_1 - C_4 -alkylene radical,

R^3 and R^4 are identical or different and are C_1 - C_4 -alkyl, and

X is O or NH.

33. The use according to any one of claims 24 to 32,
15 wherein the C_1 - C_6 -carboxylic acid is a monocarboxylic acid.

34. The use according to any one of claims 24 to 32, wherein the C_1 - C_6 -carboxylic acid is acetic acid.

35. The use according to claim 34, wherein the acetic acid contains not more than 20% by weight of water.

20 36. The use according to any one of claims 24 to 35, wherein the emulsifier is used at a strength of 2-20% by weight.

37. The use according to any one of claims 24 to 35, wherein the emulsifier is used at a strength of 5-15% by
25 weight.

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